Poptube Technology, Enabling Multifunctional Hybrid Composites for Next Generation Aircrafts

Jialai Wang, Ph.D., P.E.
Department of Civil, Construction, and Environmental Engineering
The University of Alabama, Tuscaloosa, AL35406, USA
Xinyu Zhang, Ph.D.
Department of Polymer and Fiber Engineering
Auburn University, Auburn, AL 36849

NASA Aeronautics Research Mission Directorate (ARMD)

FY12 LEARN Phase I Technical Seminar

Nov. 13–15, 2013

Outline

- The innovation
- Technical approach
- Impact of the innovation if it is eventually implemented
- Results of the LEARN Phase I effort to date
- Distribution/Dissemination—getting the word out
- Next steps

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Innovation-Poptube Technology

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- ✓ Use a novel nanoengineering technique, Poptube technology, to manufacture multiscale, multifunctional structure composites with superior mechanical performance and durability.
  - The PopTube technology is a scalable, highly energy-efficient and cost effective approach to fast grow CNTs on reinforcing fibers in large volume.

- ✓ The ultimate goal of this study is to enable practical application of CNTs in large-scale structural composites.

Why CNT Reinforcement?

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- ✓ Extraordinary mechanical properties
  - have the potential to produce much stronger and tougher materials than traditional reinforcing materials. CNT reinforcements have the potential to produce much stronger and tougher materials than traditional reinforcing materials
- ✓ Excellent thermal and electrical properties
  - provide materials with functional advantages such as
    - self-sensing abilities, flame retardancy,
    - wear resistance,
    - electrical and thermal conductivity,
    - electromagnetic interference shielding,
    - improved thermal stability

Challenges Of CNTs Reinforcement

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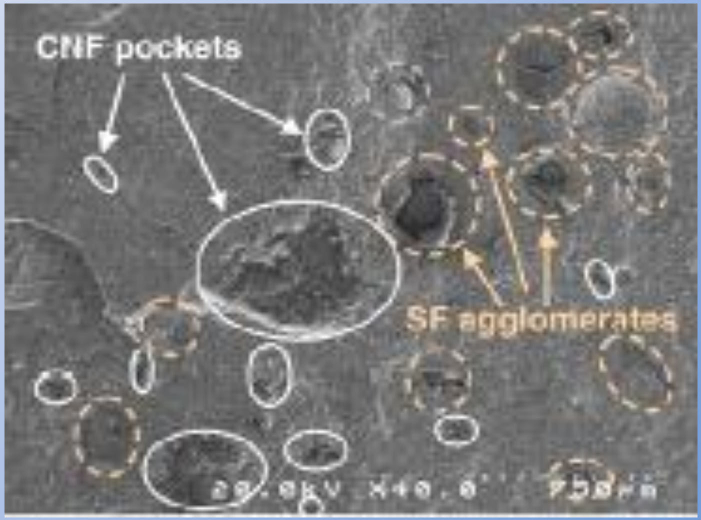
- ✓ proper dispersion of the nanoscale additives
- ✓ scale-up of laboratory results and implementation on larger scale
- ✓ Lowering the cost benefit ratio
- ✓ Effective bonding between CNTs and matrix



SEM image showing poor dispersion of CNTs in matrix

Growing CNTs On Reinforcements

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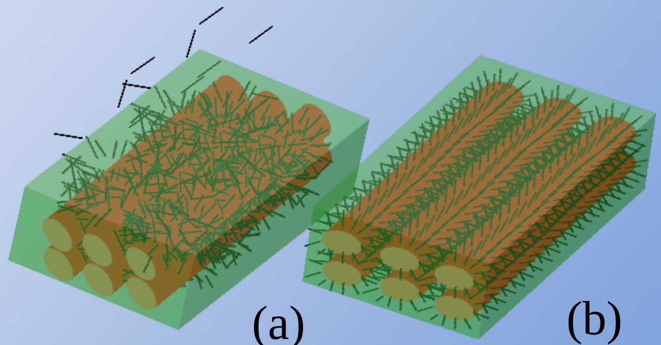
To avoid difficulty of dispersion CNTs, CNTs can be grown on the fibers.

- ✓ The CNTs are radially aligned around the fiber. This alignment is ideal to reinforce the transverse direction of the FRPs. The alignment can also prevent micro-buckling of the fiber, which is a critical failure mode of the fiber under compression.



CNT reinforcing schemes: (a) CNTS dispersed in matrix; (b) CNTS attached to fibers

- ✓ The stress transfer between the fiber and the matrix is improved significantly due to the increased surface area, mechanical interlock, and local stiffening created by the CNTs on the fiber.

- ✓ The time-consuming multistep process of purification and functionalization of CNTs is eliminated, leading to a significant reduction of cost.

Methods to Incorporate CNTs with Reinforcements

- ✓ Chemical Vapor Deposition (CVD) method
  - Can damage the fiber
    - Tensile strength can be reduced up to 50%
  - Non-continuous process
    - difficult to scale-up

- ✓ Deposit CNTs onto fibers by using
  - electrophoretic deposition
  - dip coating,
  - a nanocomposite polymer sizing
  - chemical method:covalently graft functionalized carbon fibers
    - Loss some advantages on transverse reinforcement, low bond strength between CNTs and fibers.

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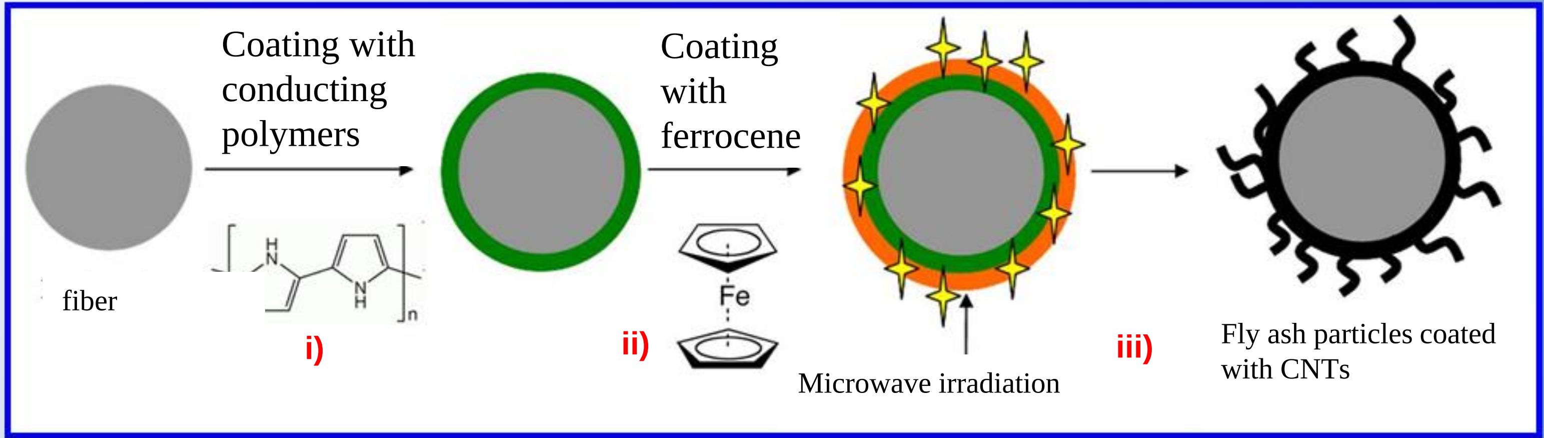
Poptube Technology-working Principle

- Three elements in manufacturing CNTs:
  - Reaction temperature, carbon source, and catalyst

- Poptube Technology:
  - Reaction temperature – microwave heating
  - Carbon sources and catalyst - ferrocene



Growing CNTs on a Fiber Using Poptube Technology

CNTs Grown On Fly Ash And Glass Fabrics

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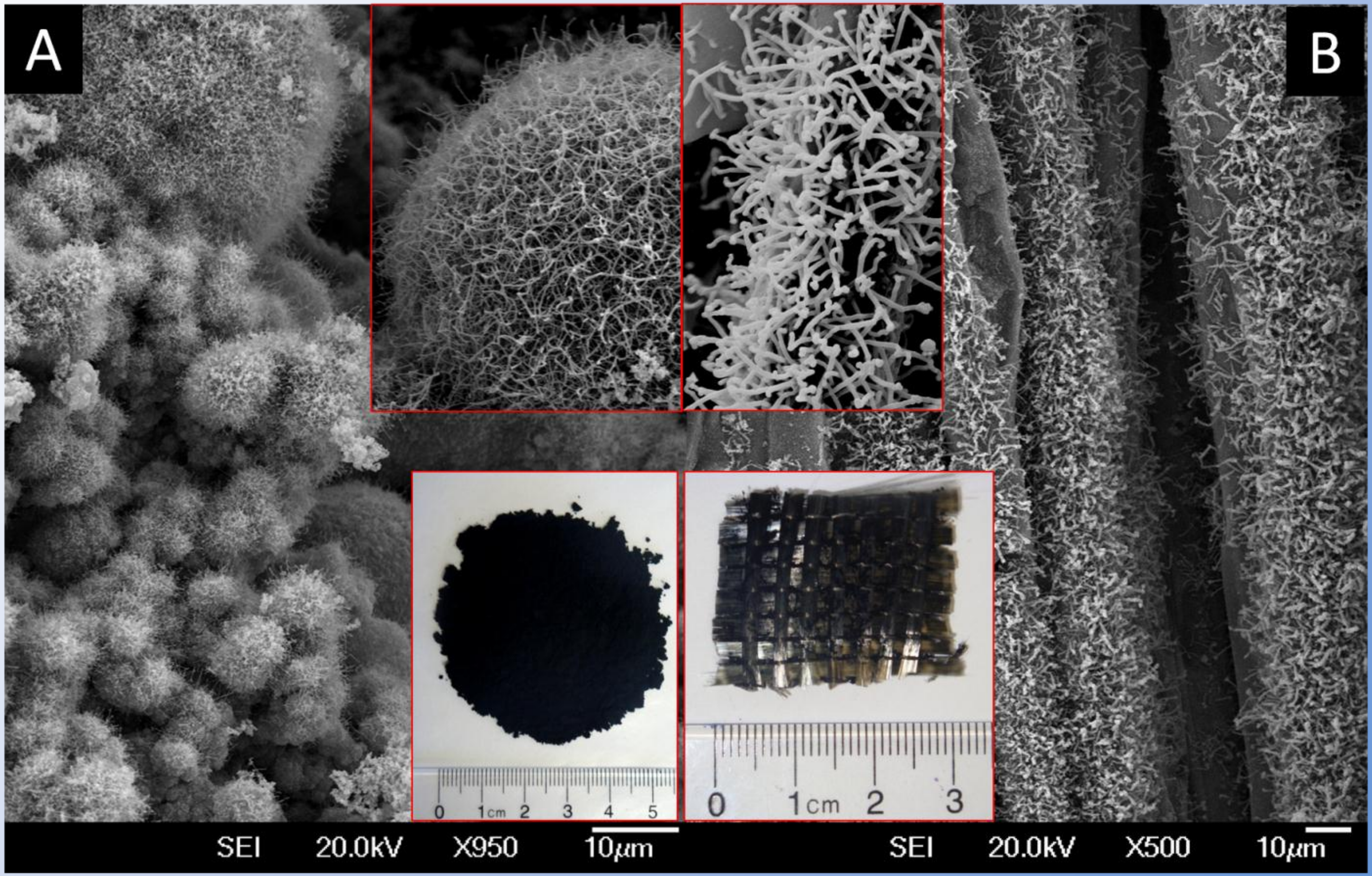

Fig 3. SEM images of as produced CNTs on (A) fly ash, insets: (top) zoom-in SEM image of the CNTs on fly ash; (bottom) digital picture of 10 g fly ash-CNT nanocomposite; and (B) glass fiber fabrics, inset: (top) zoom-in SEM image of the CNTs on glass fiber fabrics; (bottom) digital picture of 1 inch × 1 inch glass fiber fabric-CNT nanocomposite.

HTEM Image of Produced CNTs

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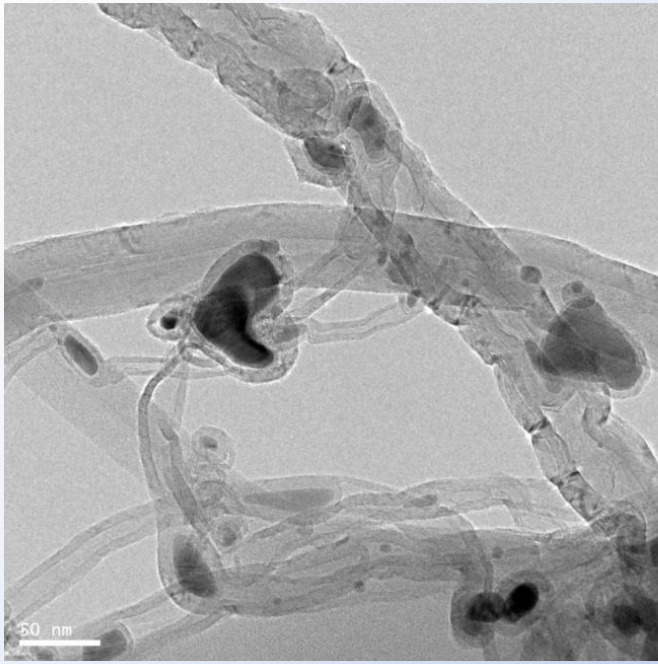

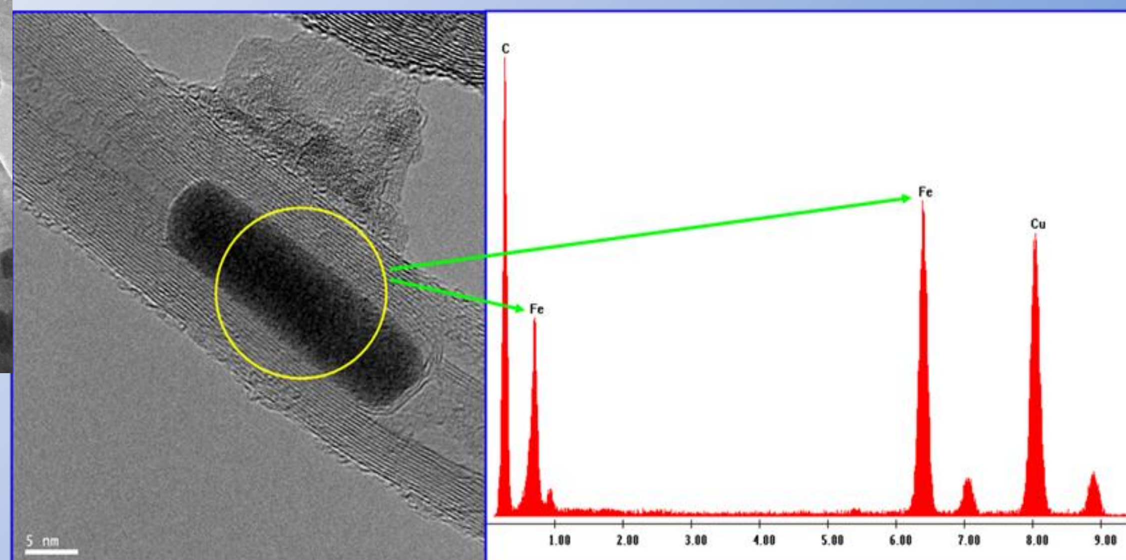

Fig 5. HRTEM image of the as-produced CNTs and EDX on selected area

Growth Mechanism Of CNTs

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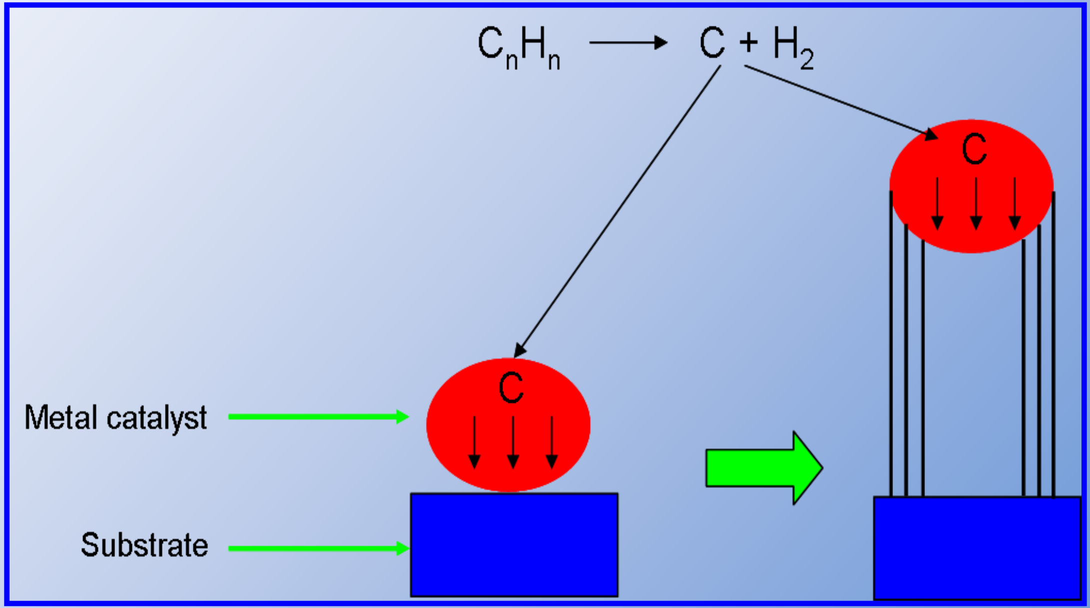
i) upon microwave heating, the conducting layer will absorb the microwave irradiation;
ii) the temperature will rise up very quickly and reach high enough to decompose ferrocene to iron and cyclopentadienyl groups.



iii. iron will stick on the surface of the heating layer, and serve as the catalyst.
iv. the carbon atoms pyrolyzed from cyclopentadienyl ligand will serve as the carbon source.

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Advantages of Poptube Tecnology

- **High energy-efficiency and low cost :**
  - Only one inexpensive chemical is employed to serve as both catalyst and carbon source.
  - Microwave heating has higher efficiency of energy transfer, compared to the traditional thermal heating methods.
- **Scalable up for large volume manufacture**
  - Rapid: (<15 seconds!)
  - Since the whole process can be carried out in the air at room temperature, there is no need of expensive vacuum setups.
- **Less Damage to fibers**

Impact of the Innovation

- Advance the existing CNT manufacturing technologies, and surface modification of engineering materials.
- Enable large-scale manufacture of the CNTs reinforced structural composites for next generation aircrafts.
  - Lighter
  - More durable
  - Multifunctional
- Elimination of high cycle fatigue (HCF) problem by tough, thermally stable materials that show significantly enhanced dynamic damping properties for engine blade vibration and sound control without degradation in the thermal stability of the materials.

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Proof-of-concept: CNTs on Carbon Fibers

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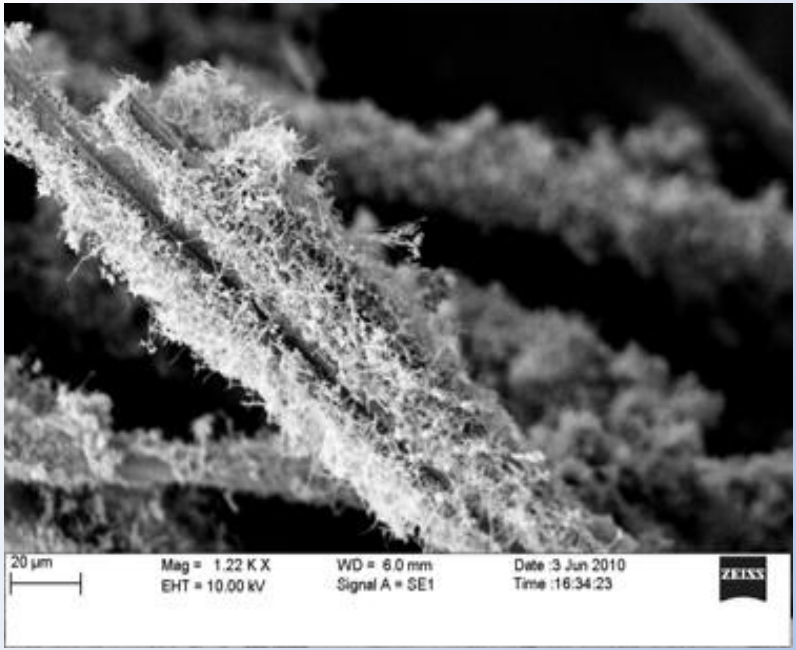

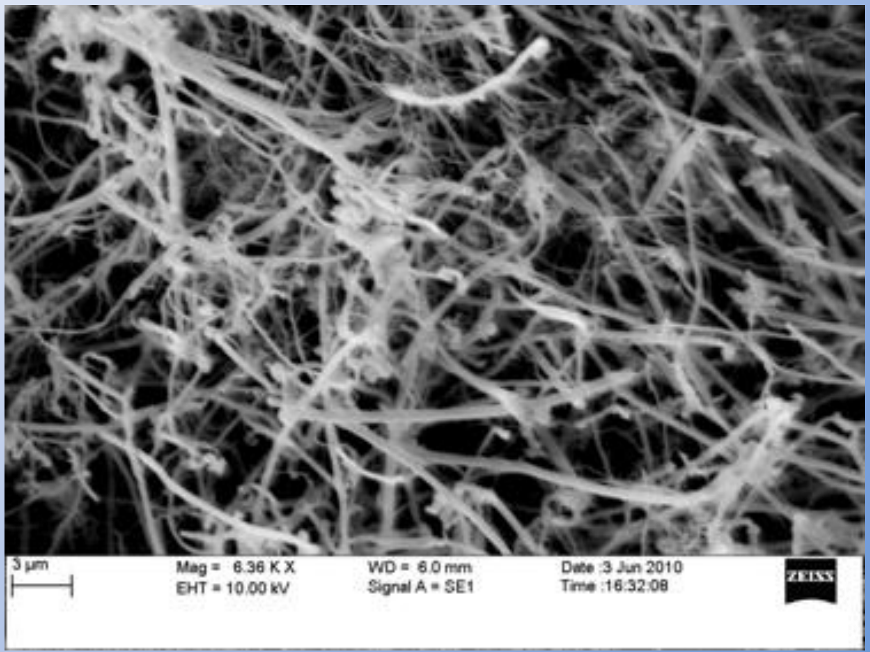

CNTs have been successfully grown on carbon fibers

Proof-of-concept: CNTs On Other Materials

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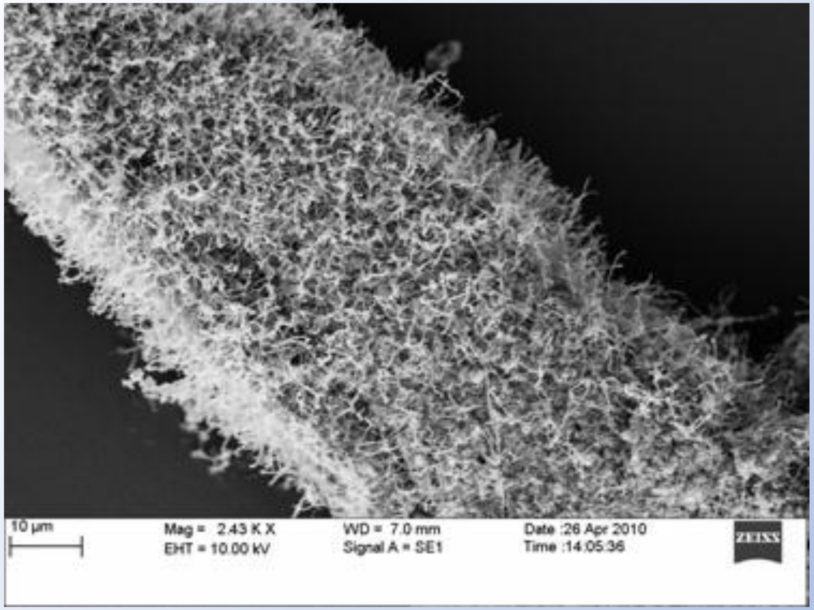
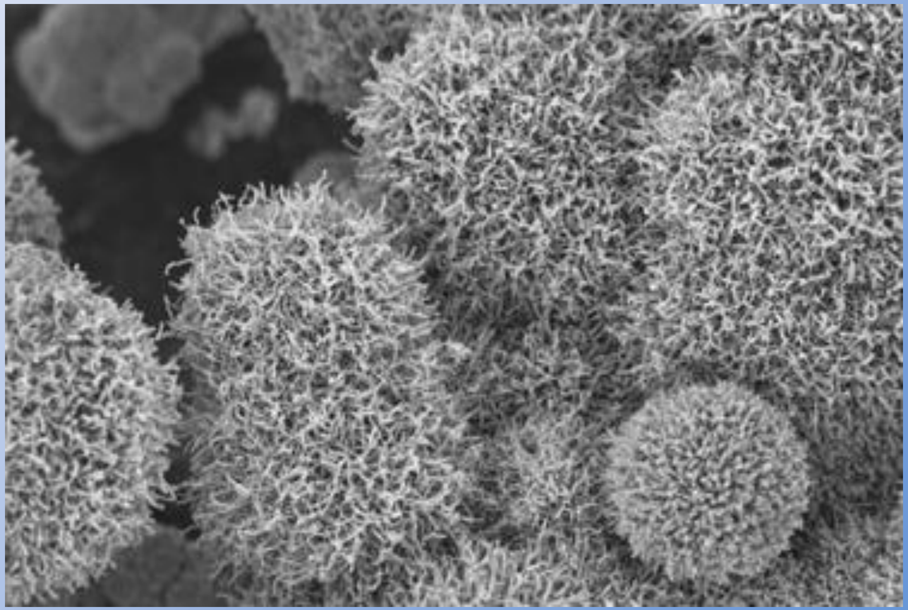


Kevlar Fibers



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Major Improvement: CNTs on Carbon Fibers

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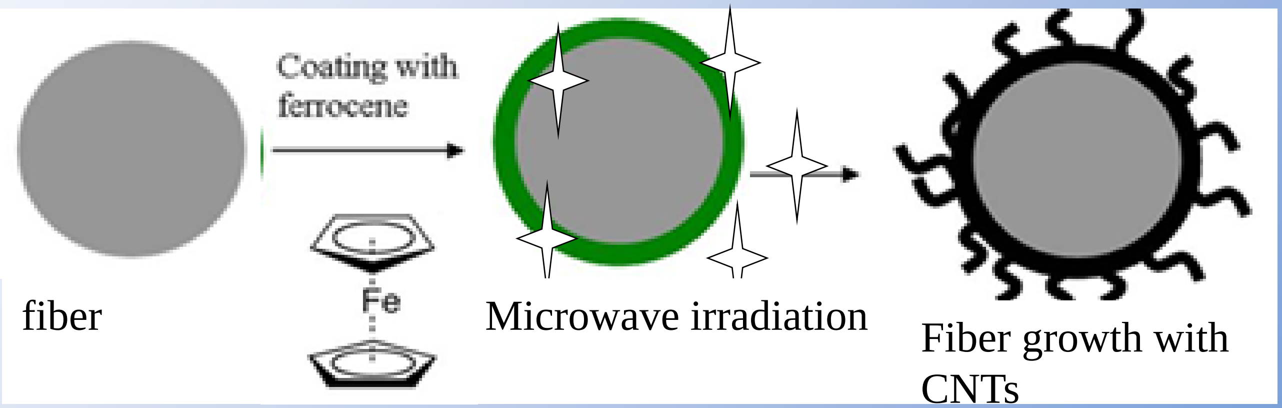
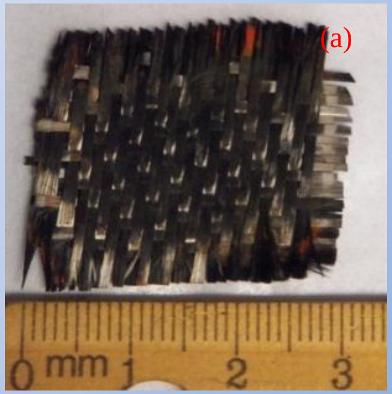
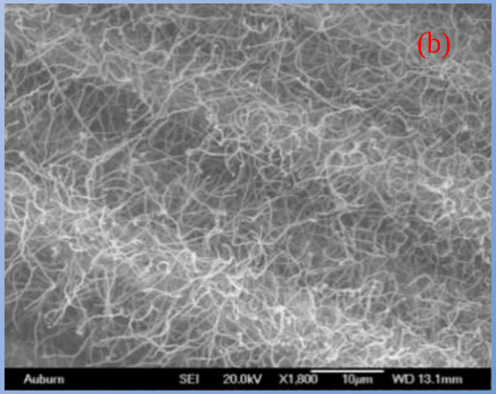
Since carbon fiber can absorb microwave energy. Conducting polymer is not needed to grow CNTs on carbon substrates! The proposed technique has been significantly simplified.

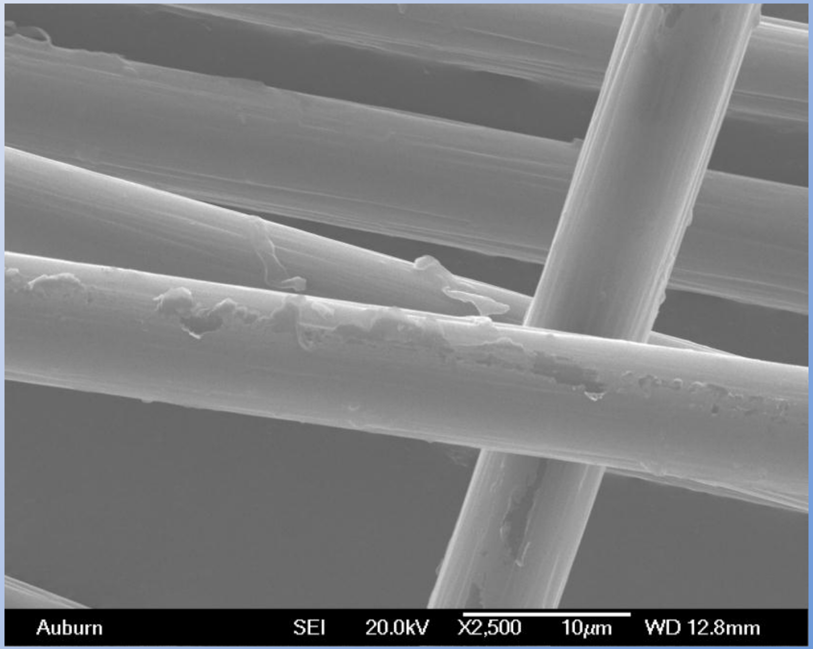






Control of CNTs Growth– Pretreatment

- ✓ Virgin CF Fabric – no treatment
- ✓ Microwave Pretreatment
  - Virgin CF fabric exposed to microwave irradiation for 1 min
- ✓ Acetone Pretreatment
  - Virgin CF fabric soaked overnight in acetone



SIGMATEX carbon fiber fabric: DV 233, Plain weave,195 g/sq.m, with silane sizing layer

Control of CNTs Growth -Processing

- ✓ After pre-treatment, CF Fabric soaked for 30 min in a 0.5 M Ferrocene-Toluene solution.
- ✓ Fabric removed from the solution and allowed to dry.
- ✓ Sample was microwaved for 45 sec.
- ✓ Hexane addition
  - Before MW, 1 mL of hexane (0.5 mL on each side of fabric) was added to 1 sample from each set (No PT, MW PT, Acetone PT)

No Pretreatment- Carbon Fiber Fabric

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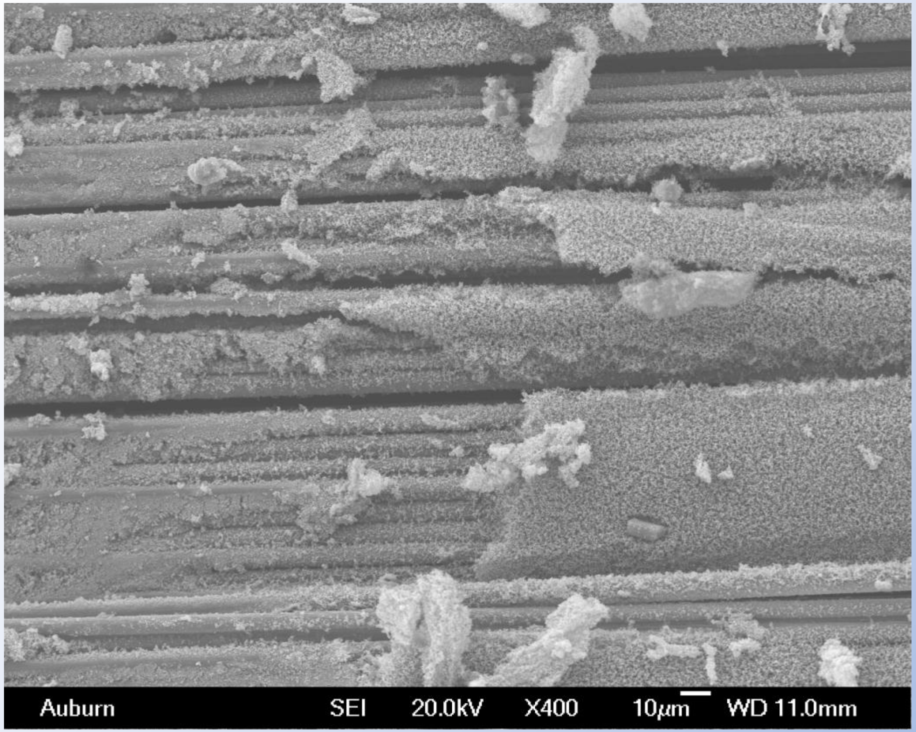
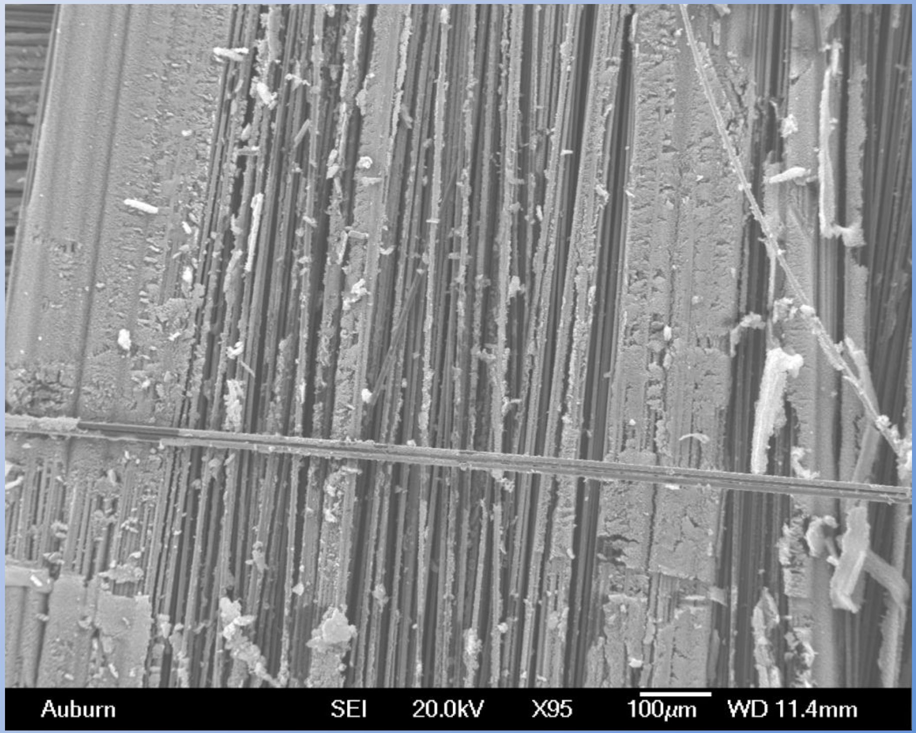
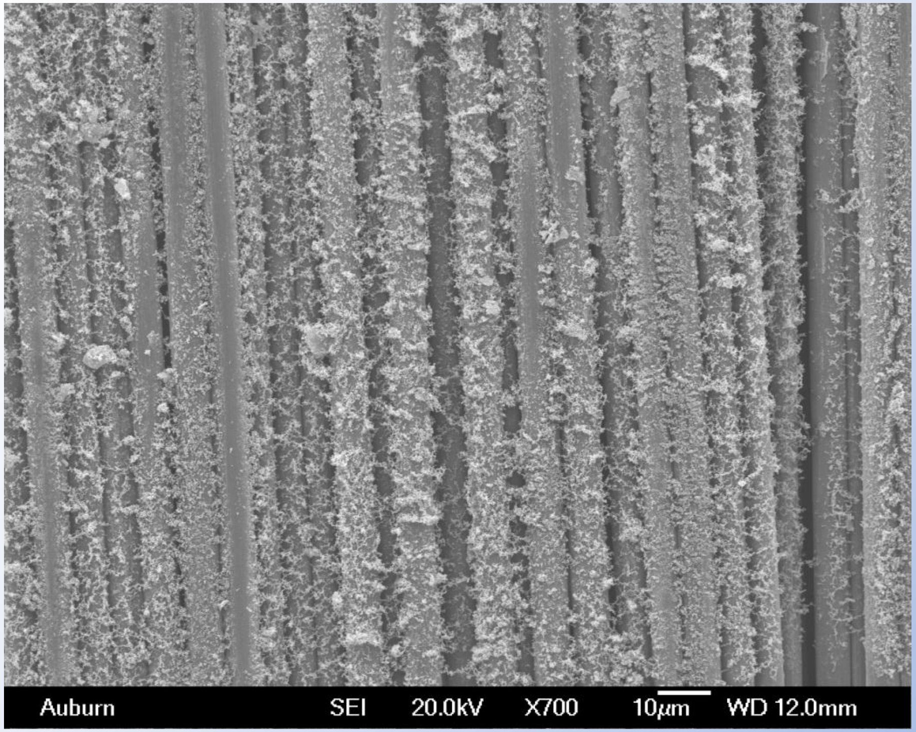
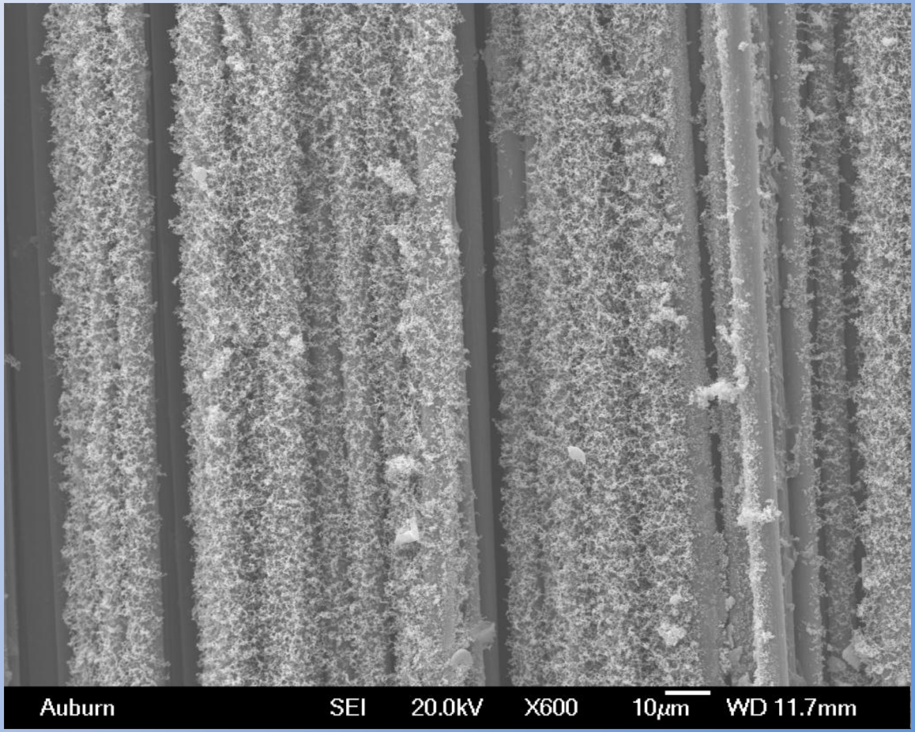




Areas of decent coverage, yet on a larger scale the coverage is relatively poor and non-uniform.

No Pretreatment-Carbon Fiber Fabric w/ Hexane





The addition of hexane improves the coverage on the CF

Microwave Pretreatment- Carbon Fiber Fabric

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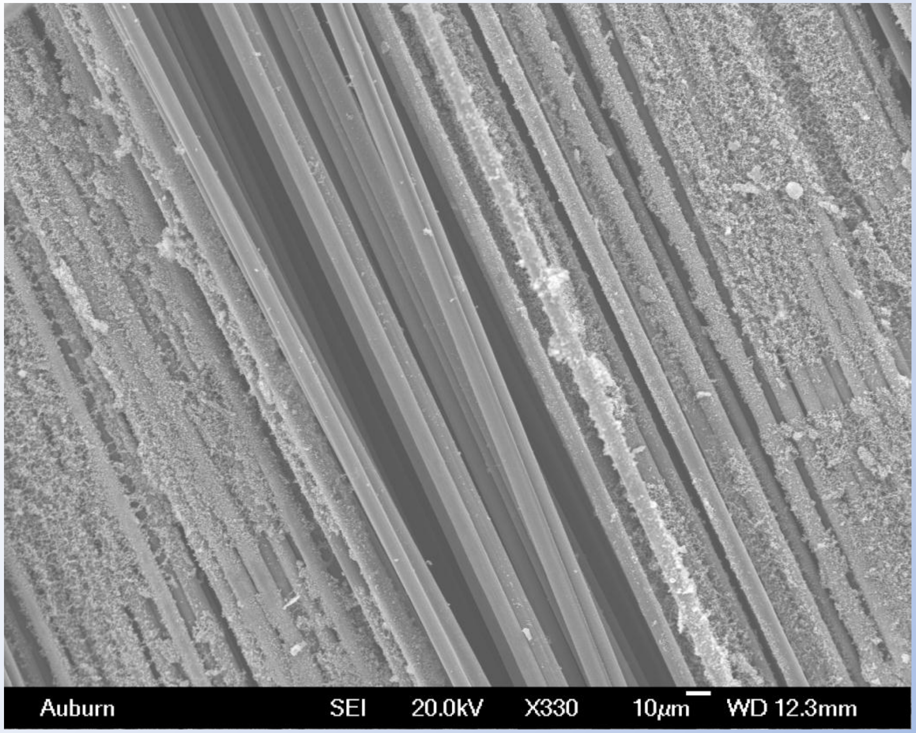

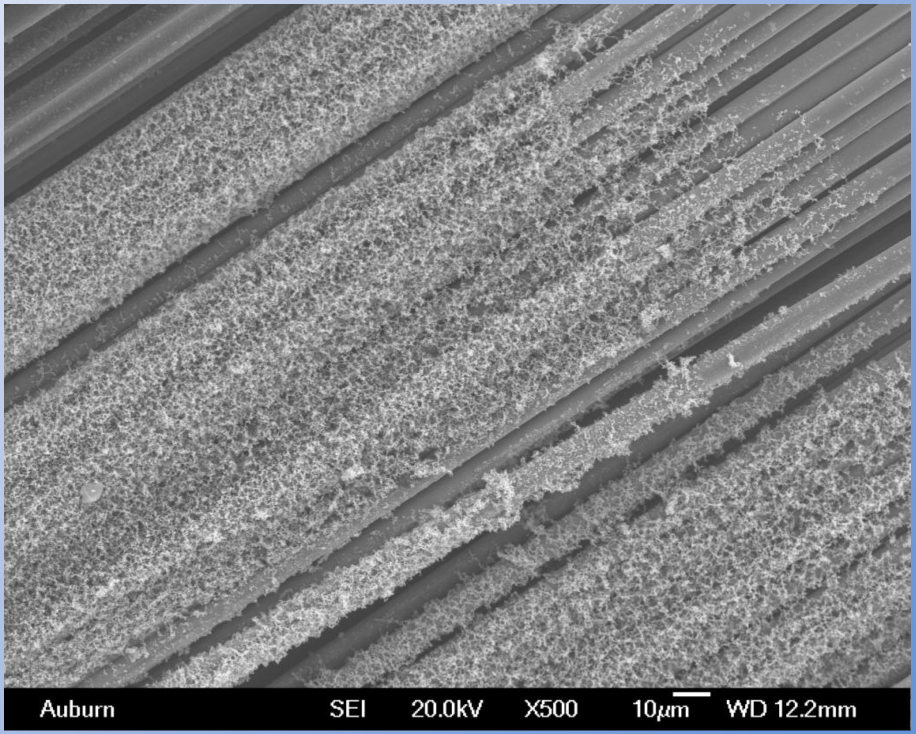

MW pre-treatment provides a much cleaner surface for attachment that translates to a better coverage and growth compared to the sample without pre-treatment.

Microwave Pretreatment- Carbon Fiber Fabric w/ Hexane

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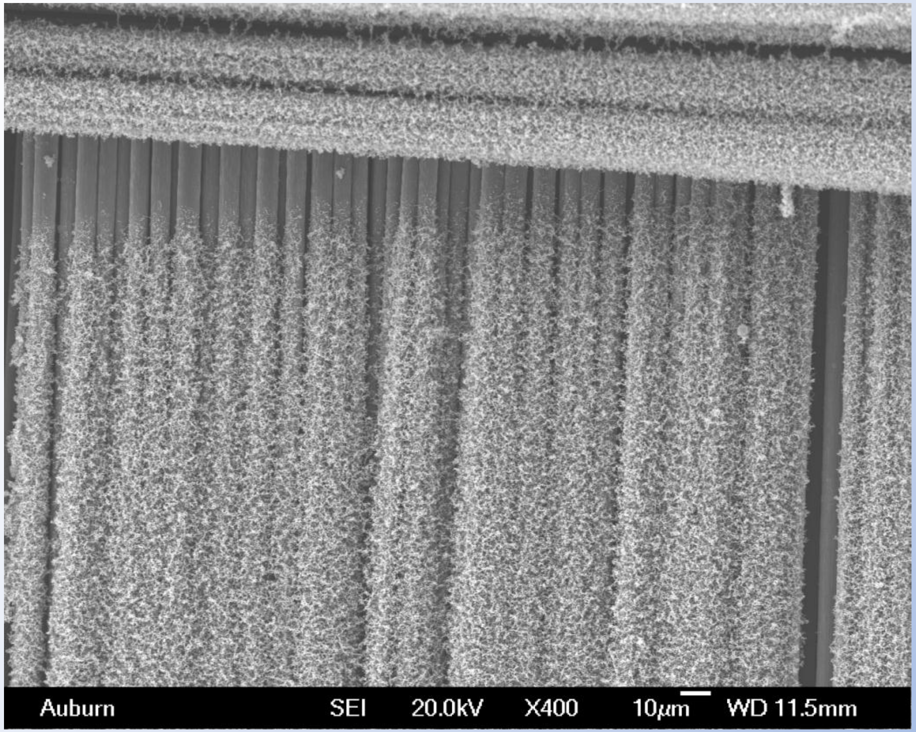

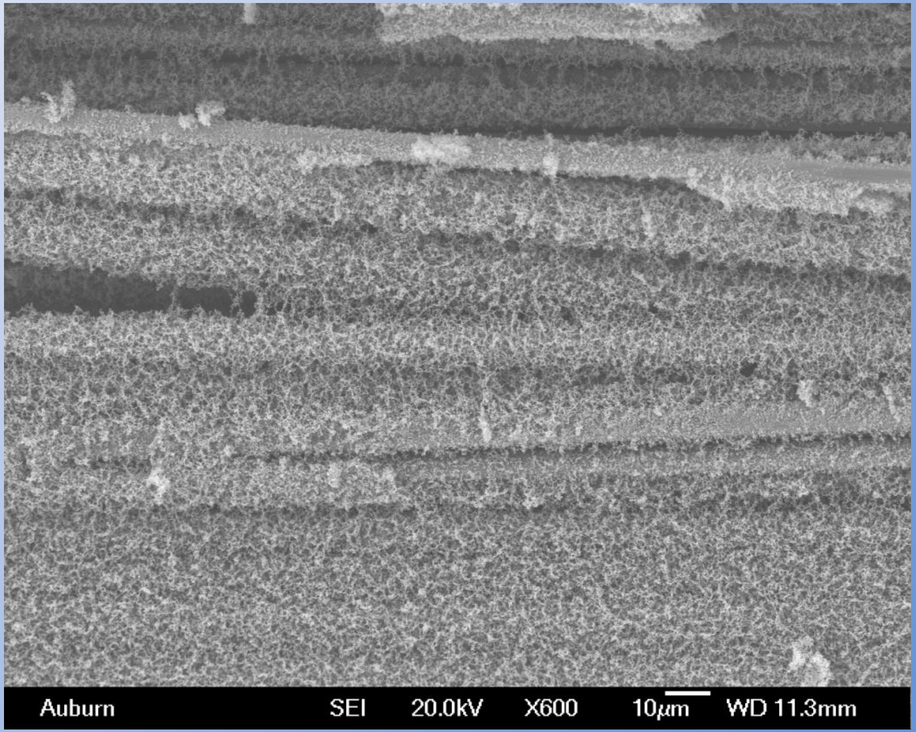

The addition of hexane improves the coverage on the MW Carbon Fiber

Acetone Pretreatment-Carbon Fiber Fabric

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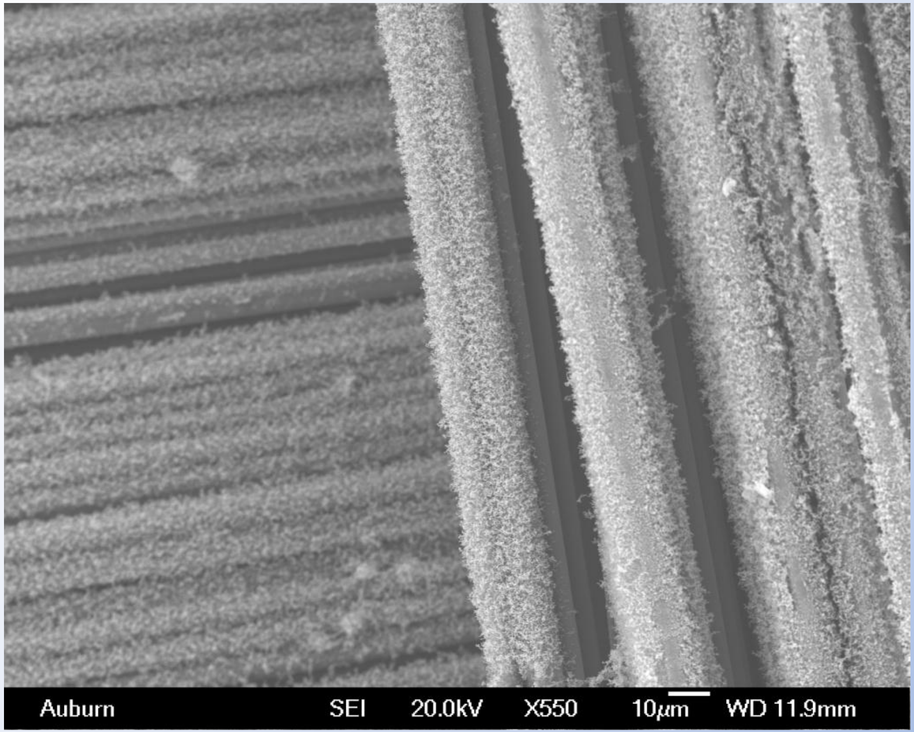

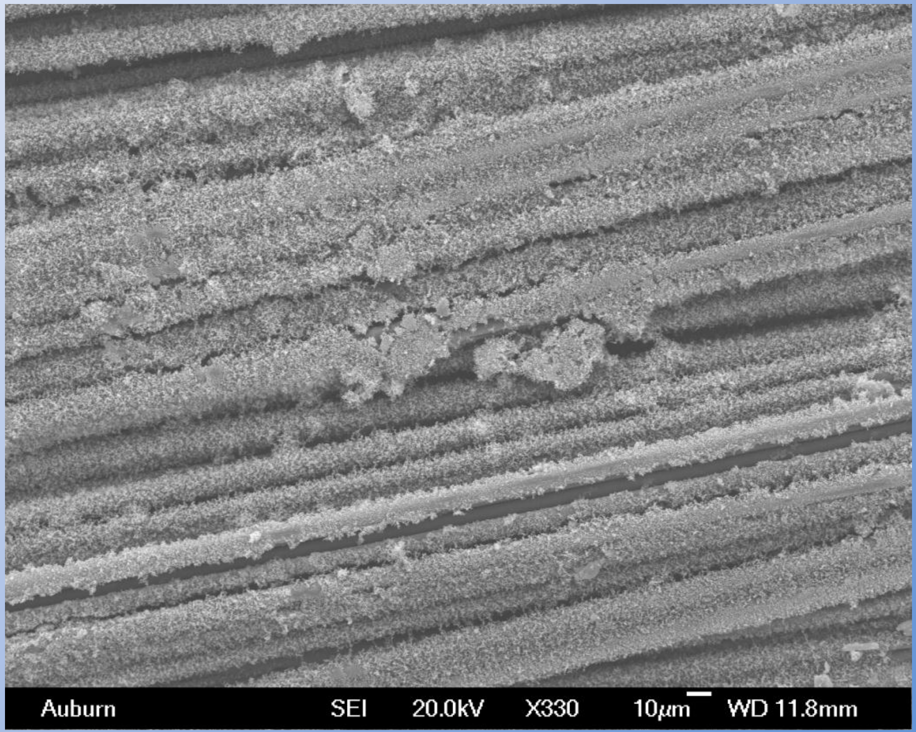

This sample provides the best growth and coverage for samples that do not have the addition of hexane.

Acetone Pretreatment- Carbon Fiber Fabric w/ Hexane

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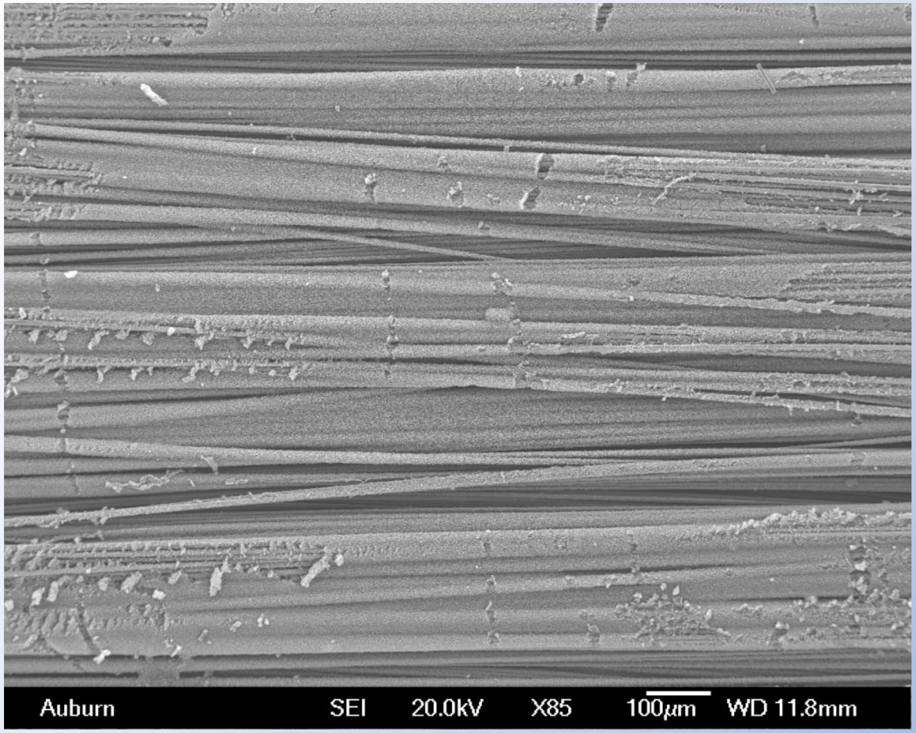
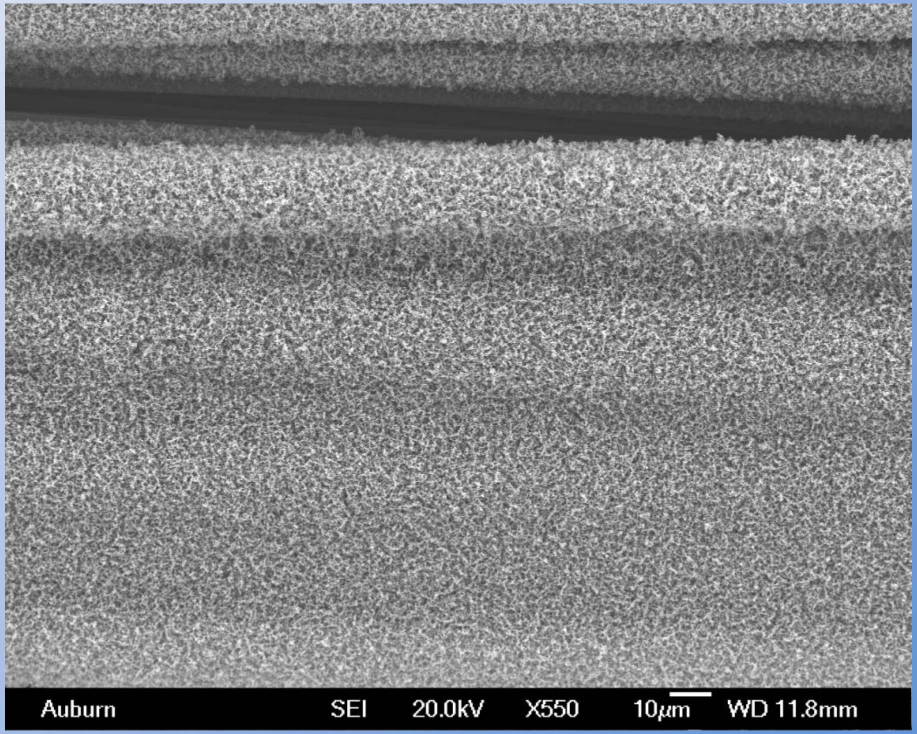
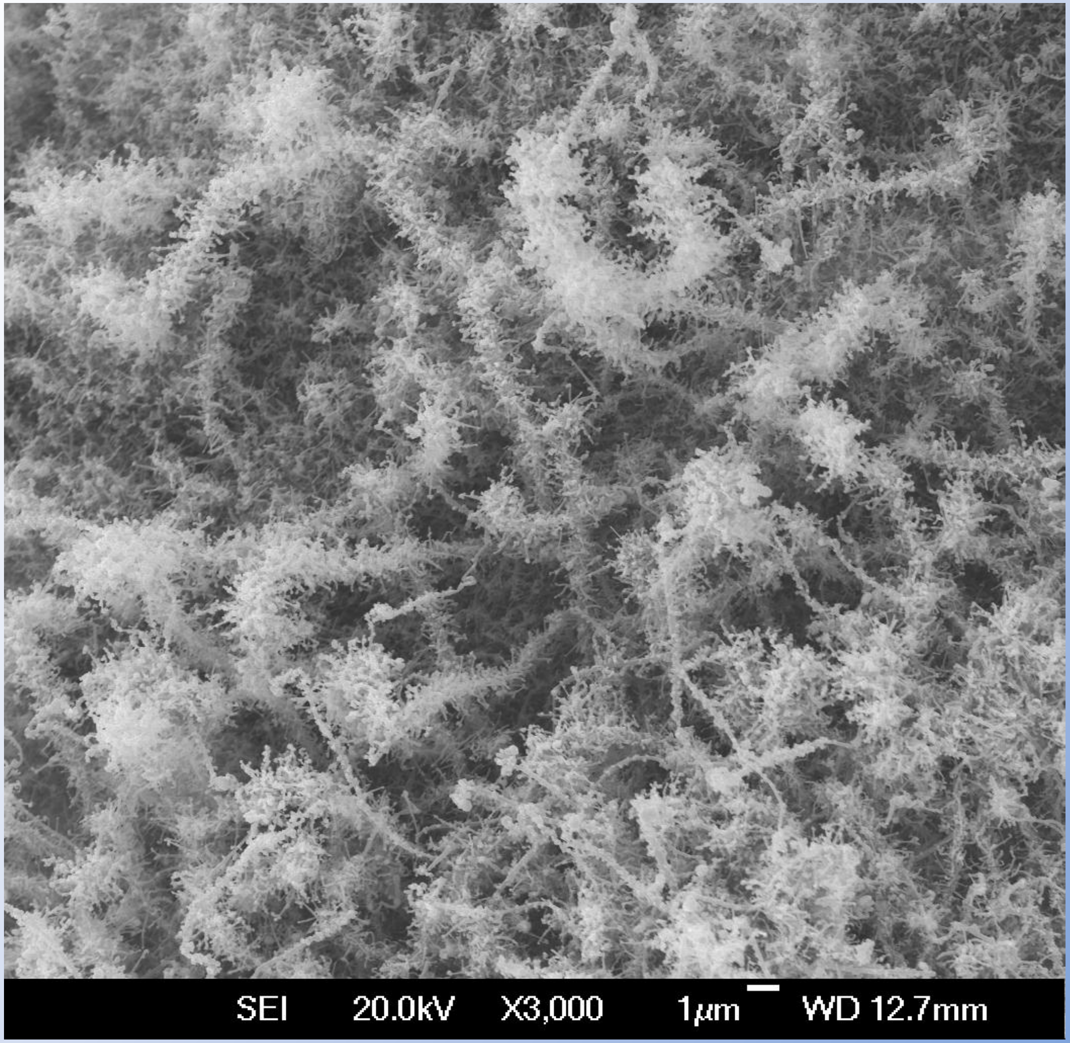




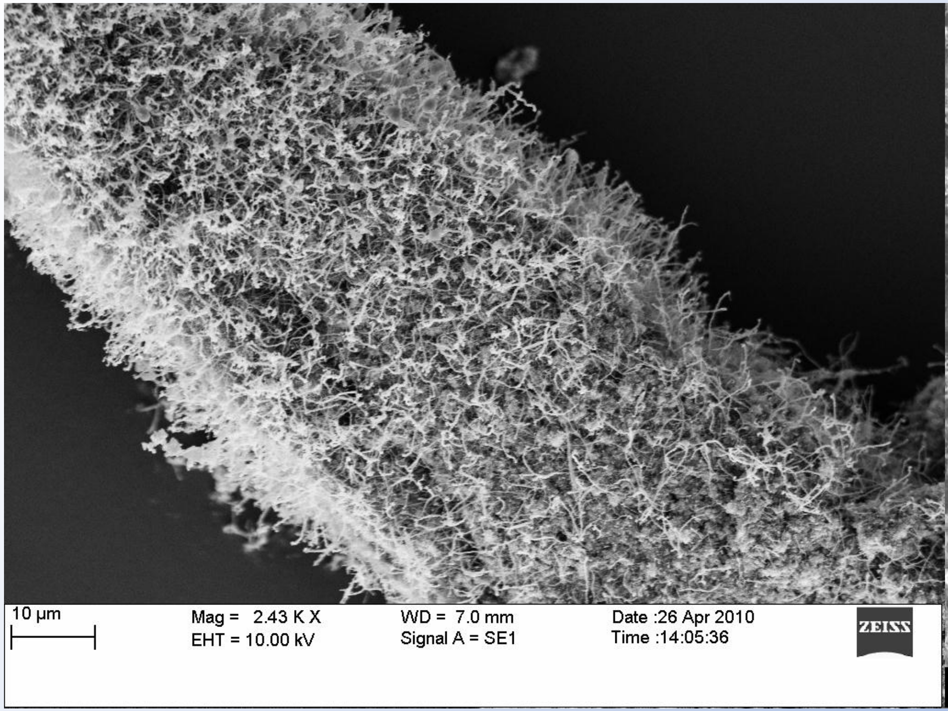
- The addition of hexane improves the coverage on the CF
- The best coverage in terms of uniformity

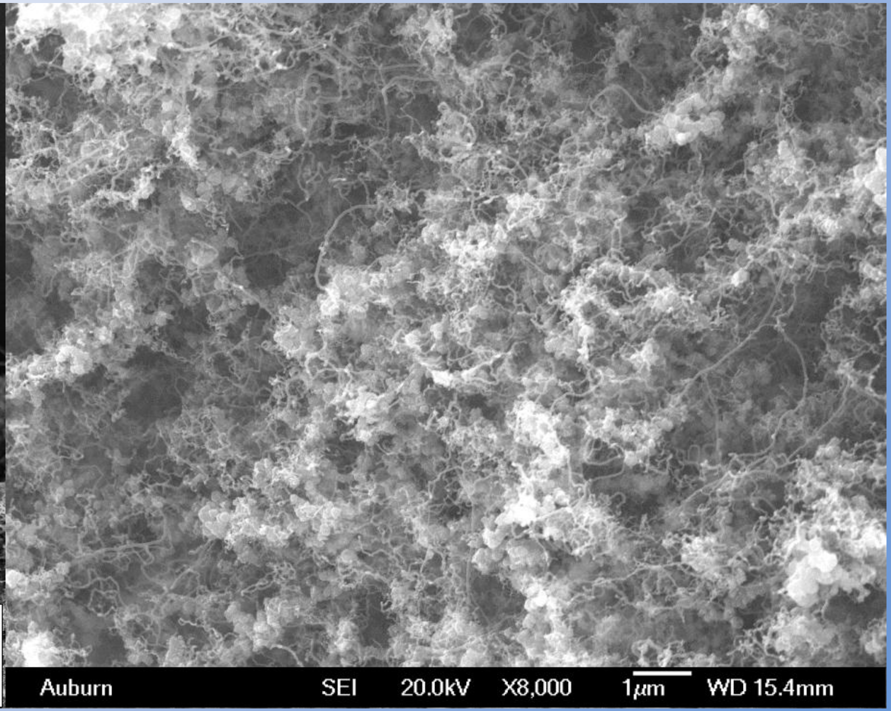
New Findings: Secondary structure growth for CNTs

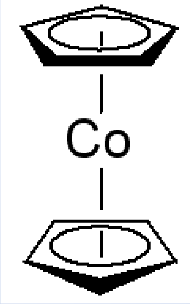


Secondary growth of CNTs to produce 3-D nanoparticles, which are more desirable than1-D CNTs to reinforce composites.

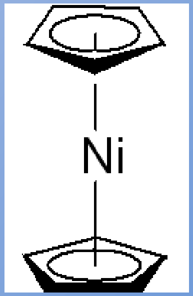
Other metallocenes







Bis(cyclopentadie nyl) cobalt (II)



Bis(cyclopentadienyl) nickel (II)

Damage On Fibers

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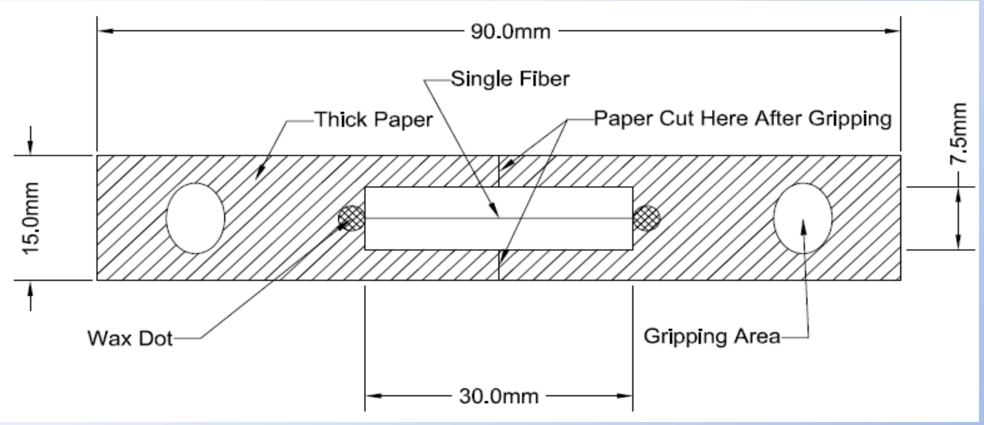
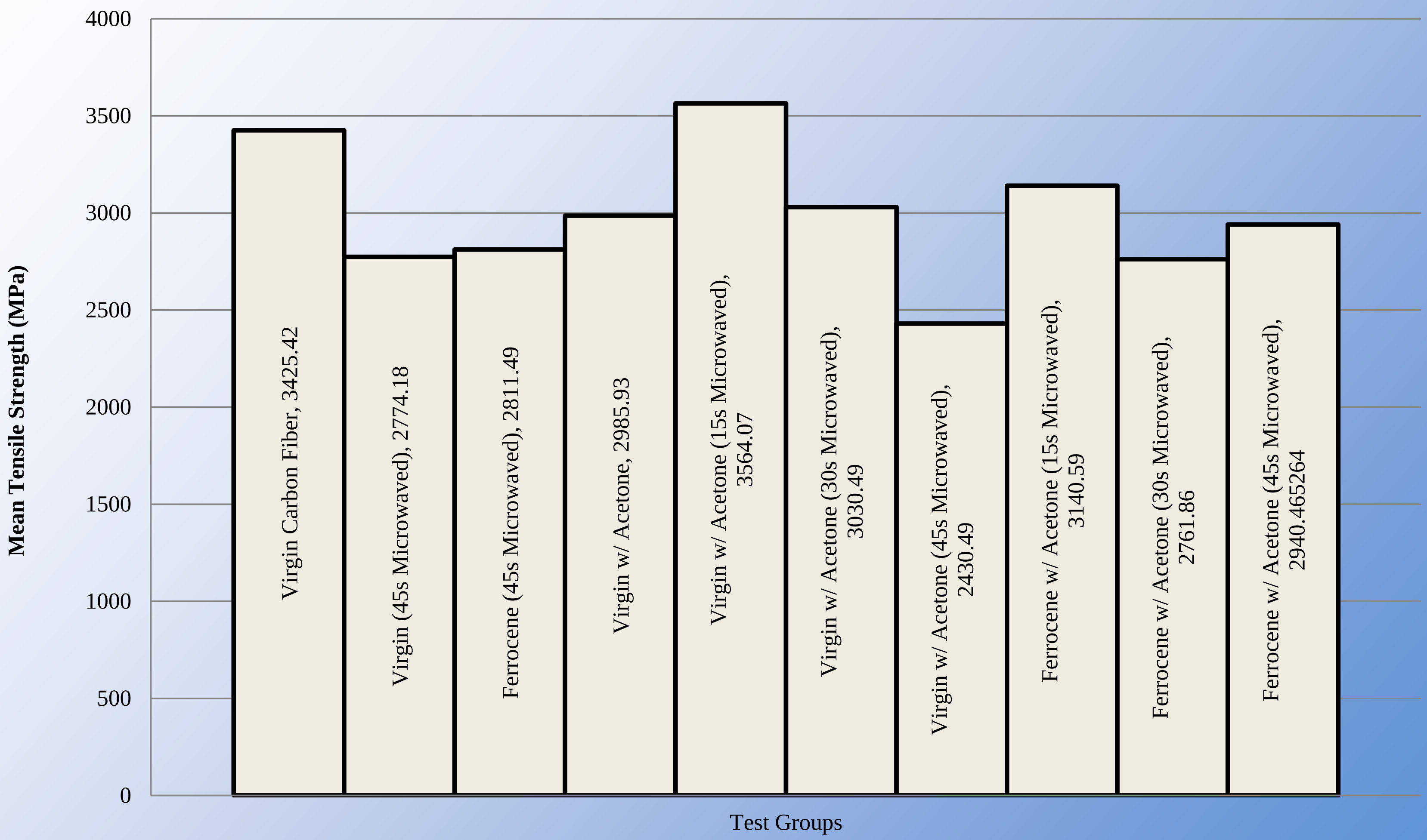


Single Fiber Tensile Tests were conducted according to ASTM D 3379-75

Single-Fiber Tensile Testing Result



Mode-I Fracture Toughness

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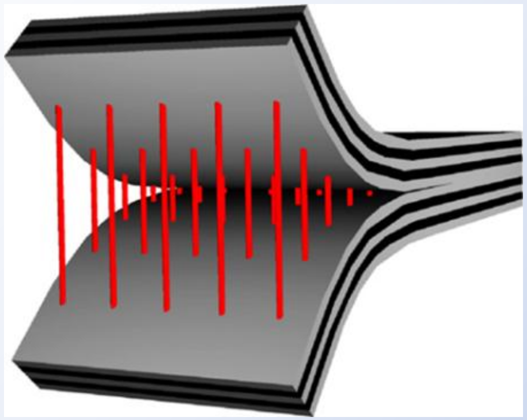

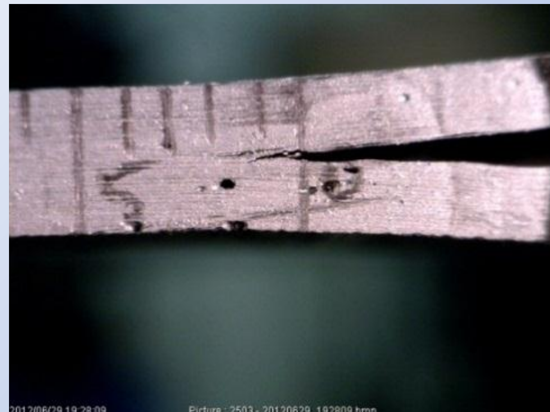

Mode I interlaminar fracture toughness measured according to ASTM D5528-01.

Specimen	AVG THICKNESS [in]	AVG WIDTH [in]	LENGTH [in]	TEMP/ HUMIDITY [º F/ % RH]	G_{IC} [KJ/m²]	G_{IC} AVG
Fabrics without CNTs	0.126	1.001	5.5	78 º F/55%	0.6967	
	0.133	1.002	5.5	78 º F/55%	0.6395	
	0.135	1.001	5.5	78 º F/55%	0.6882	0.6748
Fabrics with CNTs	0.113	1.001	5.5	78 º F/53%	0.9977	
	0.118	1.001	5.5	78 º F/53%	0.9550	
	0.122	1.001	5.5	78 º F/53%	0.9706	0.9744

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Distribution/Dissemination

- Jialai Wang, Xinyu Zhang, 2013. Enable carbon nanotube reinforcement in infrastructure material using Poptube Approach. Presented at Engineering Mechanics Institute Conference, ASCE, August 4-7, 2013.

- Jialai Wang, Xinyu Zhang, 2013. Poptube Technology: Enabling Next Generation Multiscale and Multifunctional Structural Composites. ASC 28th annual technical conference, Sept 9th – 11th, 2013, State College, PA, CD-ROM proceeding (9 pages).

- Jialai Wang, Xinyu Zhang, Will Guin, 2013. Manufacture of Hierarchical, Multifunctional Structural Composites Using a Novel Scalable and High Energy-efficiency Nanoengineering Technique. (Poster) Nanotechnology for Defense, Tucson, AZ, Nov. 4-7, 2013.

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Phase II- Task 1: Continuous Manufacturing

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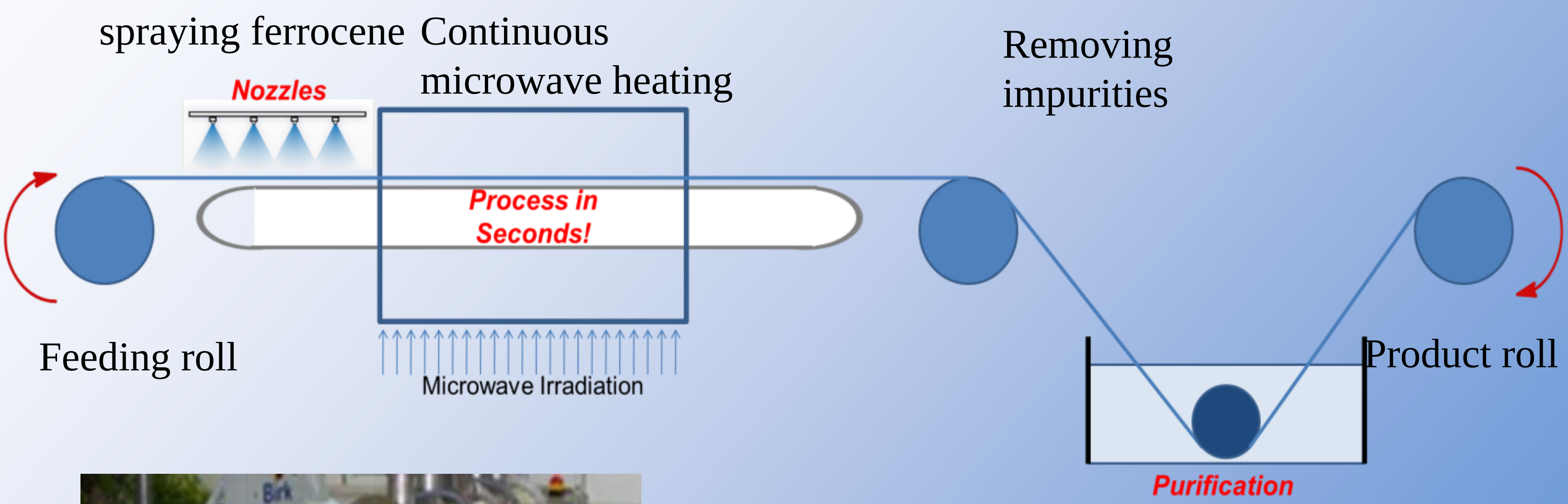

Scale up the proposed technique in phase I to a continuous process using a Microwave Continuous Belt Heater (MCBH) purchased from Linn High Therm (Germany) at a rate of 80 m^2/hr.

Continuous Manufacturing - Prepregs

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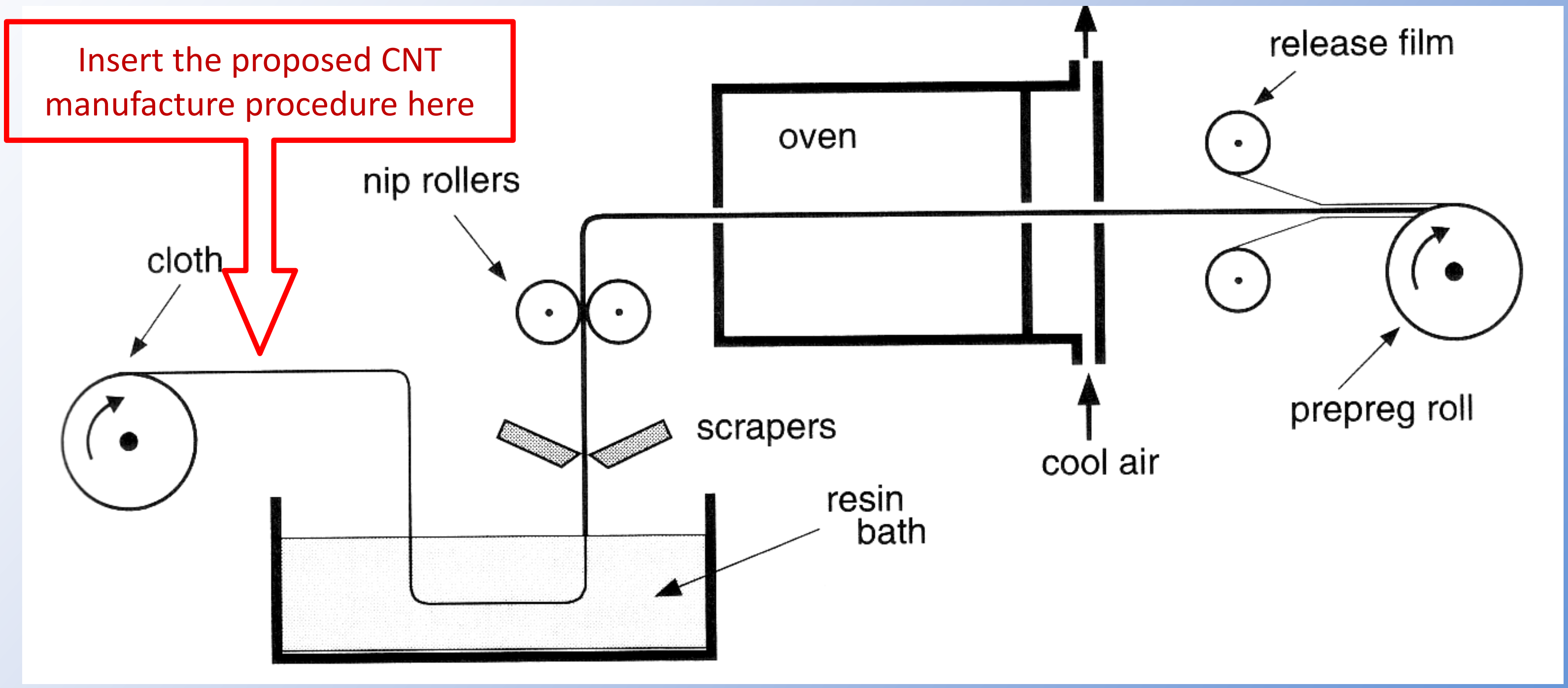

Continuous Manufacturing - Pultrusion

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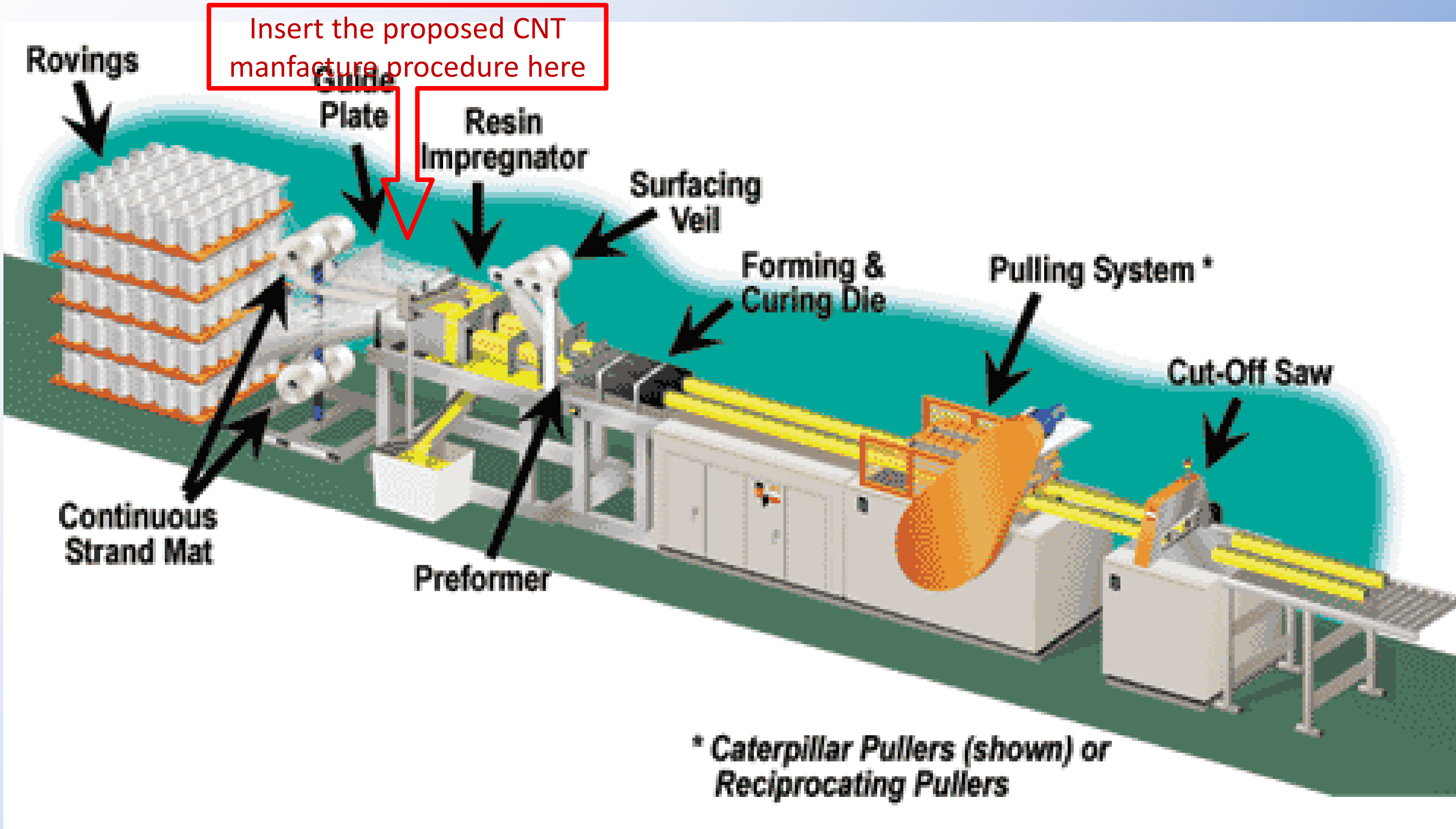
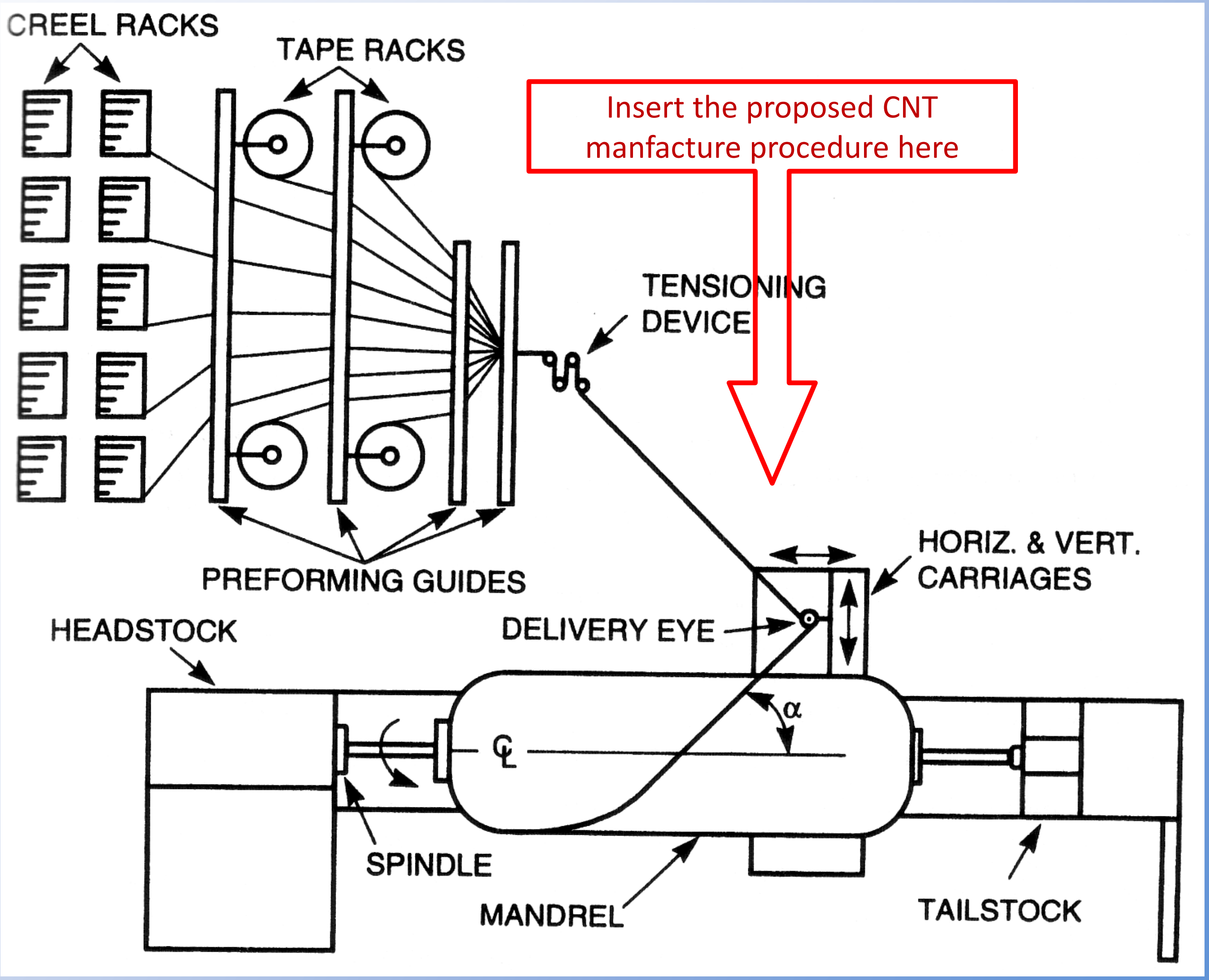


Continuous Manufacturing - Filament winding



Phase II-Task 2: Determine bond strength between CNTs and fibers

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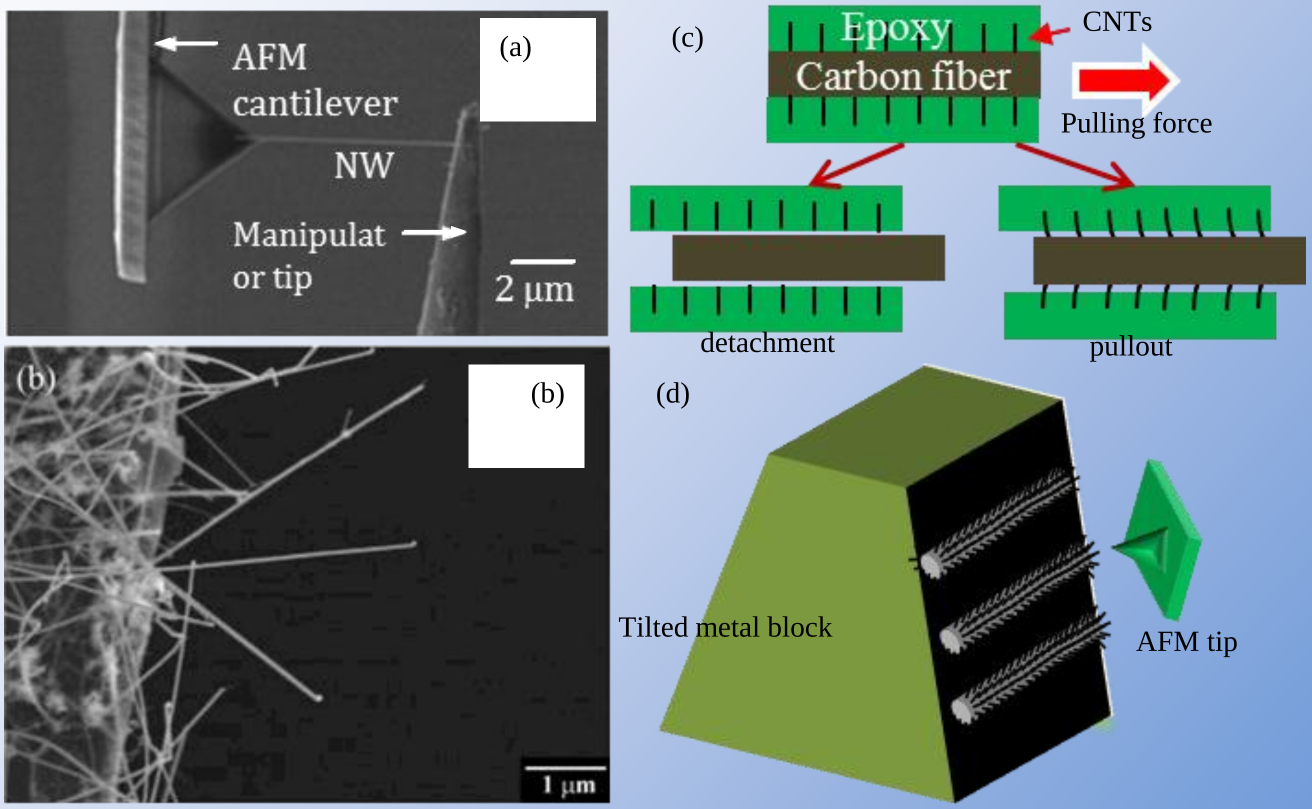


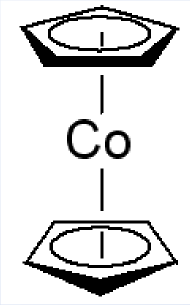
(a) Experimental setup of the in-situ SEM nanomechanical testing including the nanomanipulator tip (actuator) and the AFM cantilever (load sensor). (b) As-prepared samples with single NWs protruding for subsequent manipulation and testing. (c) Two major interface failure modes in the hybrid composite. (d) Proposed experimental setup to measure the bond strength between CNTs and carbon fibers

Phase II-Task 3: Improve bond strength between CNTs and fibers

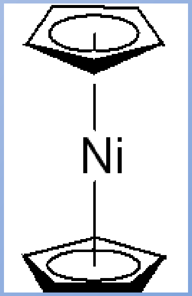
- To avoid damaging the tensile strength of carbon fibers, several possible methods will be carefully selected to make least impact to the mechanical strength of carbon fibers, but to adjust the surface chemistry of the carbon fibers for a better bond between CNTs and carbon fibers.
  i. hydrazine reduction treatment to remove some of the oxygen functional groups;
  ii. oxidation technique to induce carboxylic acid group on the surface of carbon fibers;
  iii. short-term microwave treatment;
  iv. conducting polymer coating.

Phase II-Task 4: Reduce Damage to Carbon Fibers

- Since Fe in ferrocene can react with carbon fiber to cause possible damage in the fiber, different types of metallocene with transition metals other than Fe will be used to grow CNTs.
  - For example, transition metals like Co, Ni and V can be chosen to replace Fe, to form different metallocenes with a general structure, M(C5H5)2, where M represents different metal elements.

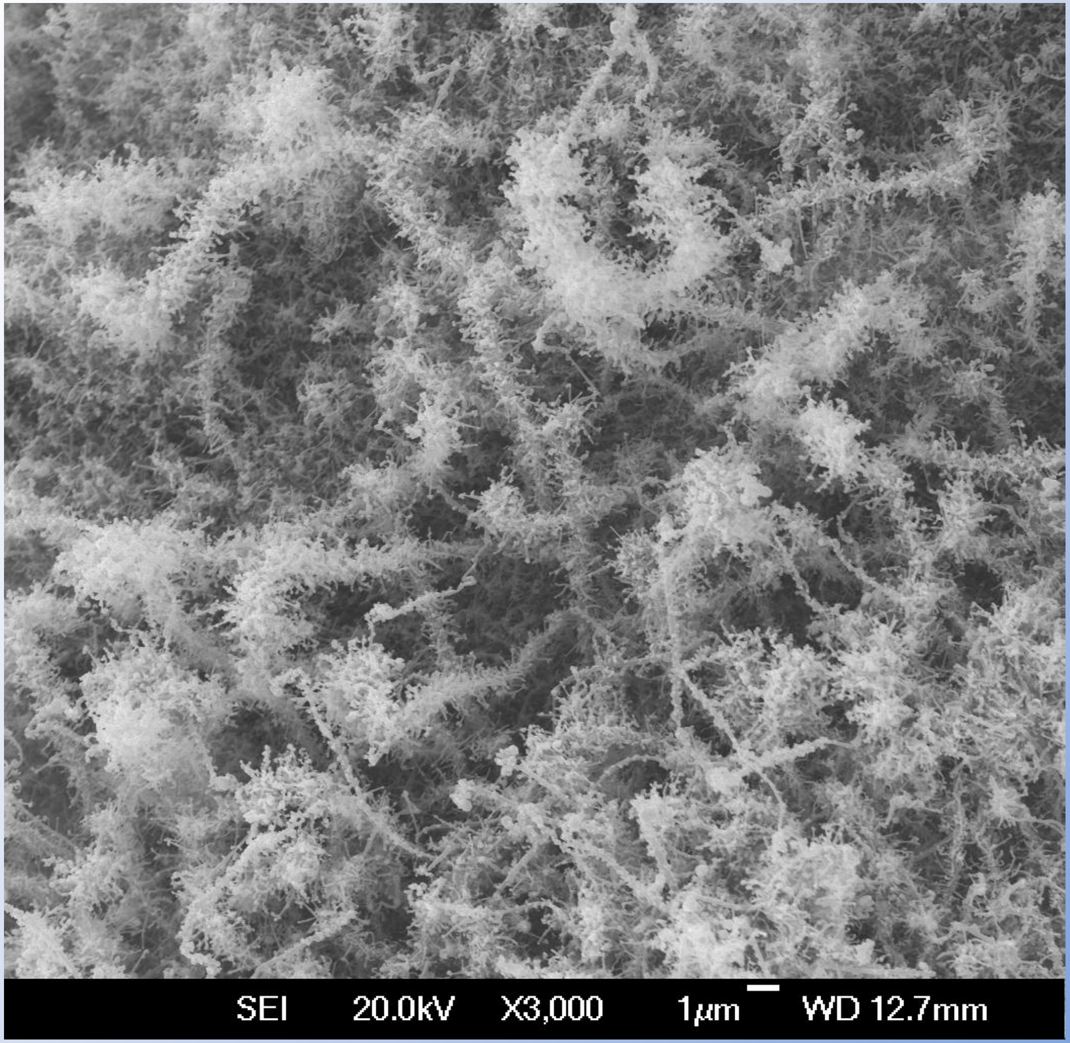


Bis(cyclopentadienyl) cobalt (II)



Bis(cyclopentadienyl) nickel (II)

Phase II-Task 5: Explore 3-D CNTs reinforcement



A simple method has been invented to produce 3-D nanoparticles. We'll perfect the manufacture process and evaluate its reinforcement effect..

Research Team

- Jialai Wang, Ph.D., P.E.
  - Department of Civil, Construction, and Environmental Engineering, The University of Alabama, Tuscaloosa, AL35406.
- Xinyu Zhang, Ph.D.
  - Department of Polymer and Fiber Engineering, Auburn University, Auburn, AL 36849.
- Yong Zhu, Ph.D.
  - Associate Professor, Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, NC 27695